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Effects of Freeze/Thaw Cycles on Hydrostatically Conditioned E-Glass/J-2 Composite

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A study was performed to determine if freeze/thaw cycles of a polymer matrix composite(PMC) with high moisture content cause increased mechanical property degradation. The PMC was a 36 ply glass fiber with a thermoplast matrix. Moisture was added hydrostatically at high pressure. It was observed that freeze/thaw cycles did not appreciably decrease the maximum load. However, from short beam shear(SBS) specimens taken from the top, middle and bottom of the hydrostatically conditioned sample, the load characteristics depended on specimen location. The middle SBS specimen had a maximum load very close to

that for off the shelf dry samples.

From optical microscopy it was observed that the freeze/thaw specimens failed with multiple delaminations while the dry samples failed with single delaminations. further investigation of this observation is suggested.

INTRODUCTION

Polymer Matrix Composites (PMC's) are one group of composites that have attractive strength, strength-to-weight ratio, and stiffness properties for high performance marine structural applications. Polymer matrices are of two types, thermosets and thermoplasts. The thermoplast polymer matrix is known to absorb and diffuse less moisture because it does not contain "open molecular structures" and unsaturated sites, which react with water, a highly polar solvent, as does a thermoset matrix. Moisture absorption results in plasticization of the matrix, and subsequently to swelling which can cause matrix cracking and fiber/matrix debonding. However, in many structural applications, such as aircraft, thermosets are used despite the increase in moisture absorption, because their strength at higher temperature is the over riding requirement. For long term submerged usage, the amount of absorbed water could be enough for ice crystal formation when exposed to subzero environments. The expansion upon ice formation could cause matrix microcrack initiation. Further cycles of immersion and freezing may result in propagation of cracks through the matrix. This theory, however has been challenged by Tsotsis (1) who suggest not enough water molecules are available in the matrix to form ice.

Another important observation about water absorption in thermoset matrices reinforced with either carbon or glass was reported by Piggott (2). His experiments showed that expanding monomers reduced the amount of water absorption. He found that in pultrusions "the most effective conducting path for water was provided by voids rather than the interphase". His observation suggest another method for future studies of the effect of water absorption, namely, the introduction of artificially produced high void content to obtain localized high moisture concentration sites.

Another concern is that for PMC's with glass fibers, diffusion of the water through the composite can attack the polar interface between the glass and fiber (ie. degradation of the sizing). Most recent work in this area have been done by Juska (3). An excellent review of the effect of water absorption on the room temperature properties of carbon and glass fiber reinforced polymer composites is given by Williams (4).

Deep water structural application of PMC materials, such as, offshore platforms or remotely controlled observation vehicles (ROV's), would subject the polymer to a new environment, specifically, high hydrostatic pressure which could increase the rate of moisture absorption with consequent mechanical property degradation as suggested by Tucker and Brown in 1989 (5). Tucker and Brown observed higher moisture content in PMC's due to high hydrostatic pressure (eg. 2000 feet of seawater) with a loss of strength and stiffness for a graphite reinforced/vinyl ester composite. They attributed the degradation "due to activation of damage dependant mechanisms in the composite under pressure". From the more recent and extensive study of Williams and Gipple (6), the effect of water immersion time and pressure on composite absorption rates and mechanical properties were found to be material specific, making a singular environmental procedure for all composite material systems not possible. Their work included both thermoset and thermoplast matrices.

Environmental conditions of a freeze/thaw cycle on materials which have absorbed water under high pressure pose another concern. A ROV surfacing in the northern latitudes after an extended period of submersion would be subject to freezing then thawing when placed in a lab or upon resubmerging. The freeze part of the cycle could cause absorbed water to expand and possibly initiate microcracks in the matrix, debonding of the fiber/matrix interface or

interlaminar debonding. If this combination of effects occur on the PMC, they might increase the moisture pickup between freeze and thaw cycles under the action of high hydrostatic pressure. In order to determine if freeze/thaw cycles cause increased mechanical property degradation to PMC materials with high moisture content, the present study was performed.

EXPERIMENTAL DETAILS

Materials

The PMC utilized in this study contained unidirectional E-glass fibers with a J-2 polyamide thermoplast matrix. The semi-transparent matrix allowed for macroscopic examination of the PMC for delamination, debonding, and large voids in the matrix. None of these defects were observed in the test samples. The 36 ply E-glass/J-2 matrix samples were received as 0.50 x 4.10 x 0.14 inch coupons with unidirectional fiber orientation along the long axis of the coupon. The material had a 65% fiber volume fraction, 2.16 gm/cc density and a 160° C glass transition temperature. The void content, determined by scanning electron microscopy, was negligible.

Hydrostatic Water Conditioning

Each sample was identified, weighed, and dried a 60° C oven for 67 hours then reweighed. The samples were then hydrostatically conditioned in simulated sea water (pH 8.0, 1550 psi helium and 20° C) for a total of 359 days. To determine the rate of moisture absorbed the samples were removed twice. The samples were weighed and the simulated seawater replenished. The 1550 psig corresponds to 3500 feet of water depth. A schematic of the

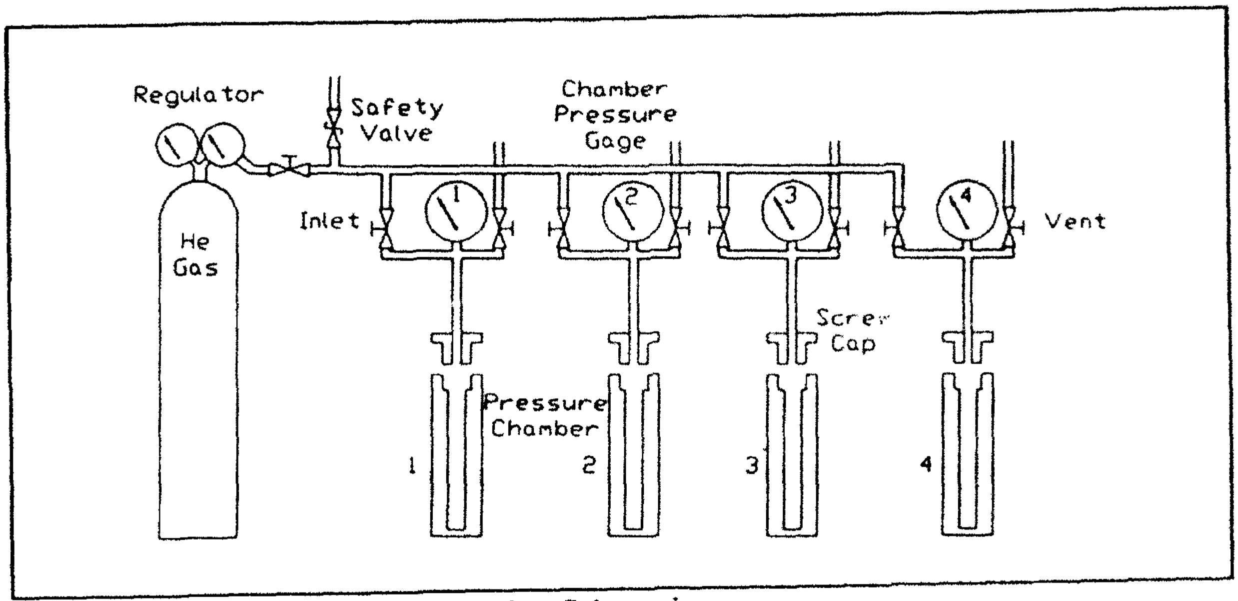


Figure 1 Multistation Pressure Chamber Schematic

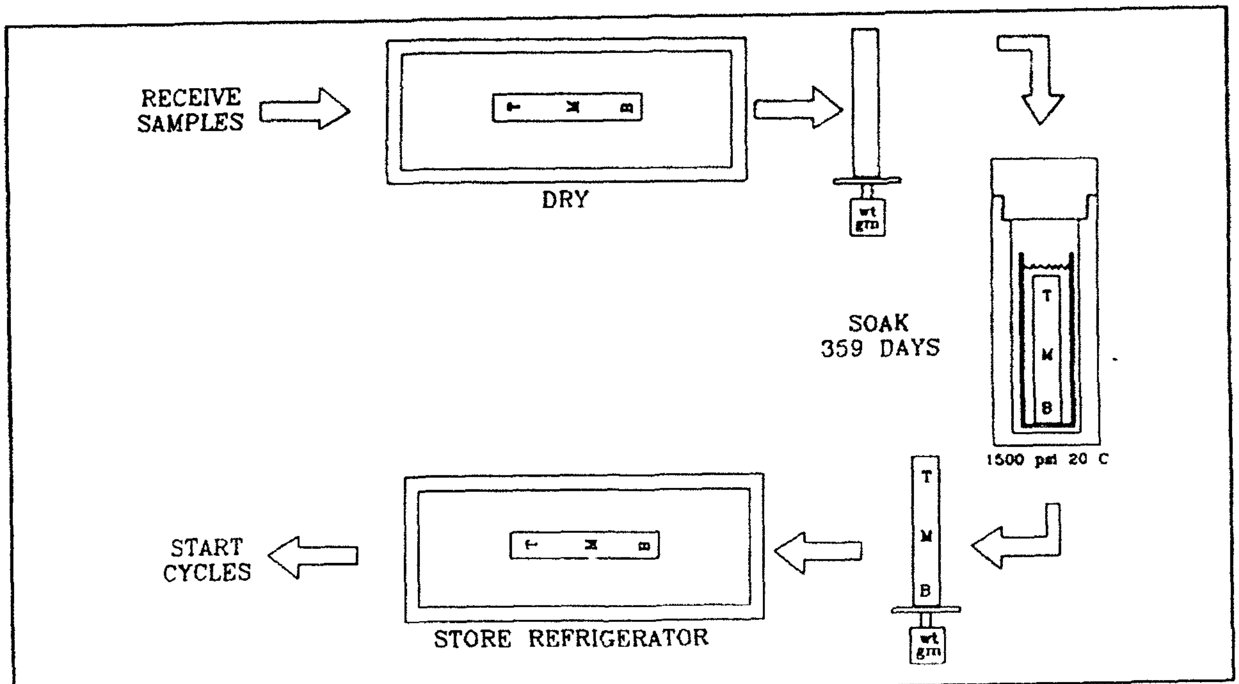


Figure 2 Hydrostatic Conditioning Process Schematic

hydrostatic conditioning apparatus is shown in figure 1. The samples were then individually wrapped in aluminum foil and placed in a refrigerator (53% relative humidity) for 69 days as depicted in figure 2. Inadvertently, all the samples were frozen during this period and upon removal from the refrigerator/freezer, they completed one freeze/thaw cycle.

Freeze/Thaw Procedure

The samples (A, B, & C) were removed from the refrigerator, dried with absorbent paper and weighted. Figure 3 shows the percent water weight of each sample with the initial point representing water weight percent immediately following the long term pressurized soak. The next point in figure 3 shows an observable drop in weight percent water due to non-immersion storage. The thaw phase cycle immersed the sample in the simulated sea water with 1550 psi pressure at room temperature for 24 hours. The samples were then removed from the pressure chamber, dried with absorbent paper, weighed, sealed in a plastic bag, and then placed either in a 7° C chamber, relative humidity 53% (sample B) or a -5° C ,relative humidity 63% (samples A & C) for 24 hours for the freeze phase. The samples were then removed from the temperature chambers and let warm or thaw at room temperature for one hour before removal from the plastic bag, dried, and weighed. These two phases completed one freeze/thaw cycle. As indicated in figure 4 the samples were next placed back into the saltwater pressure chamber for 24 hours and the cycle repeated. Sample relative position (top, middle or bottom) was maintained for every cycle to obtain any possible geotropic or bottom contact effects.

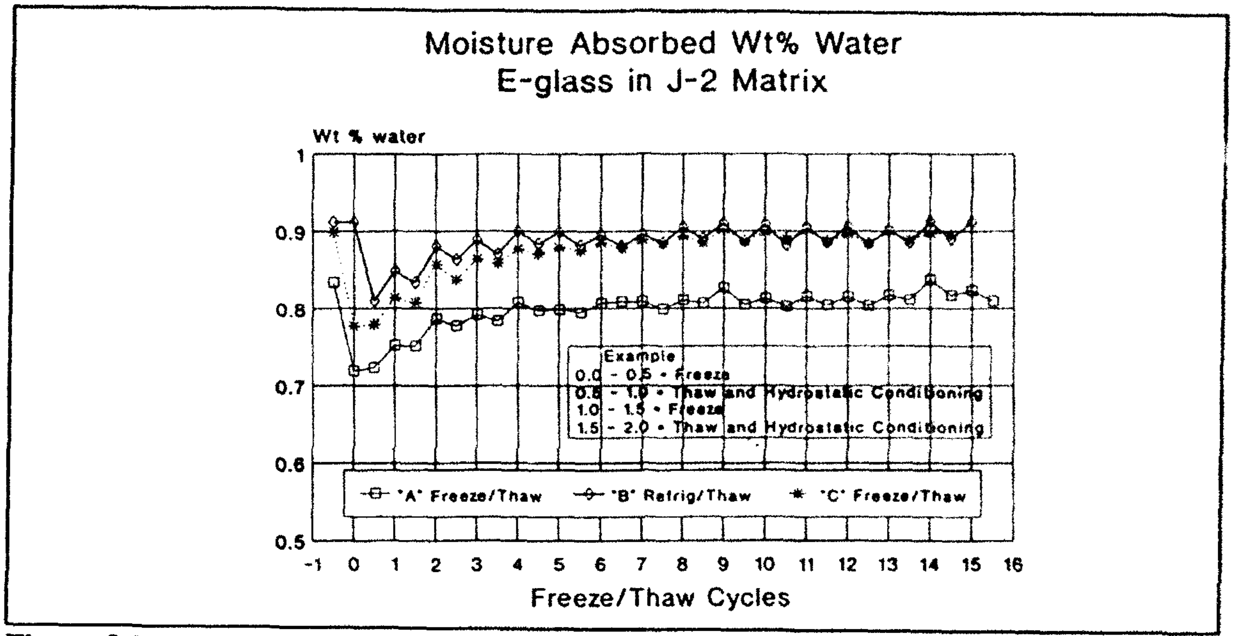


Figure 3 Percent Water Weight versus Freeze/Thaw Cycles

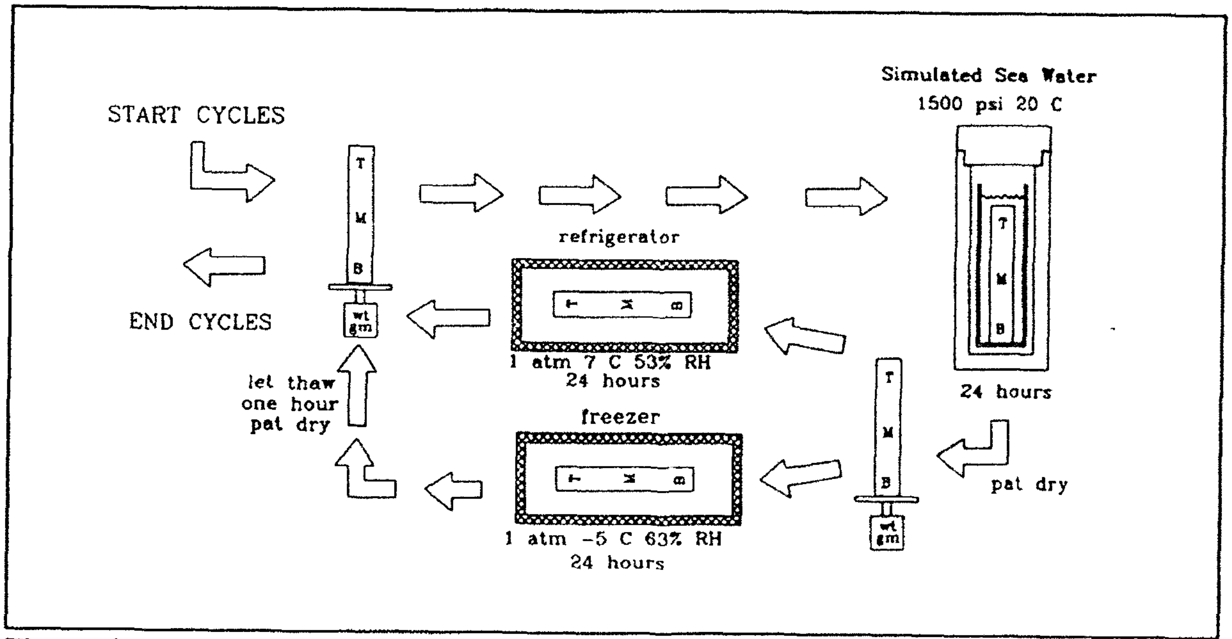


Figure 4 Freeze/Thaw Process Schematic

Dry Control Samples

Three untreated samples were cut from an "off the shelf" unsoaked non-freeze thaw cycle sample to provide control load versus deflection curves.

Load Testing

Following 15 complete freeze/thaw cycles on the samples, they were cut into 1.3 inch lengths with a water lubricated diamond saw for short beam shear (SBS) tests. Sample relative position was maintained for all short beam shear tests. The three point flexure test specimens had a span of one inch with the head speed 0.05 inches per minute.

Fractography

Fractographic features were observed by optical microscopy.

RESULTS

Moisture Absorbed

As shown in figure 5, the rate of moisture absorbed in weight percent water is linear as a function of the square root of time in days for 1500 psig of helium. This result is indicative of Fickian diffusion. The weight percent absorption is similar for that reported for the J-2.

Short Beam Shear Tests

Figure 6 shows the traces of load versus deflection for each section of the 15 cycle freeze/thaw sample C. The load versus deflection curves were very similar in shape and

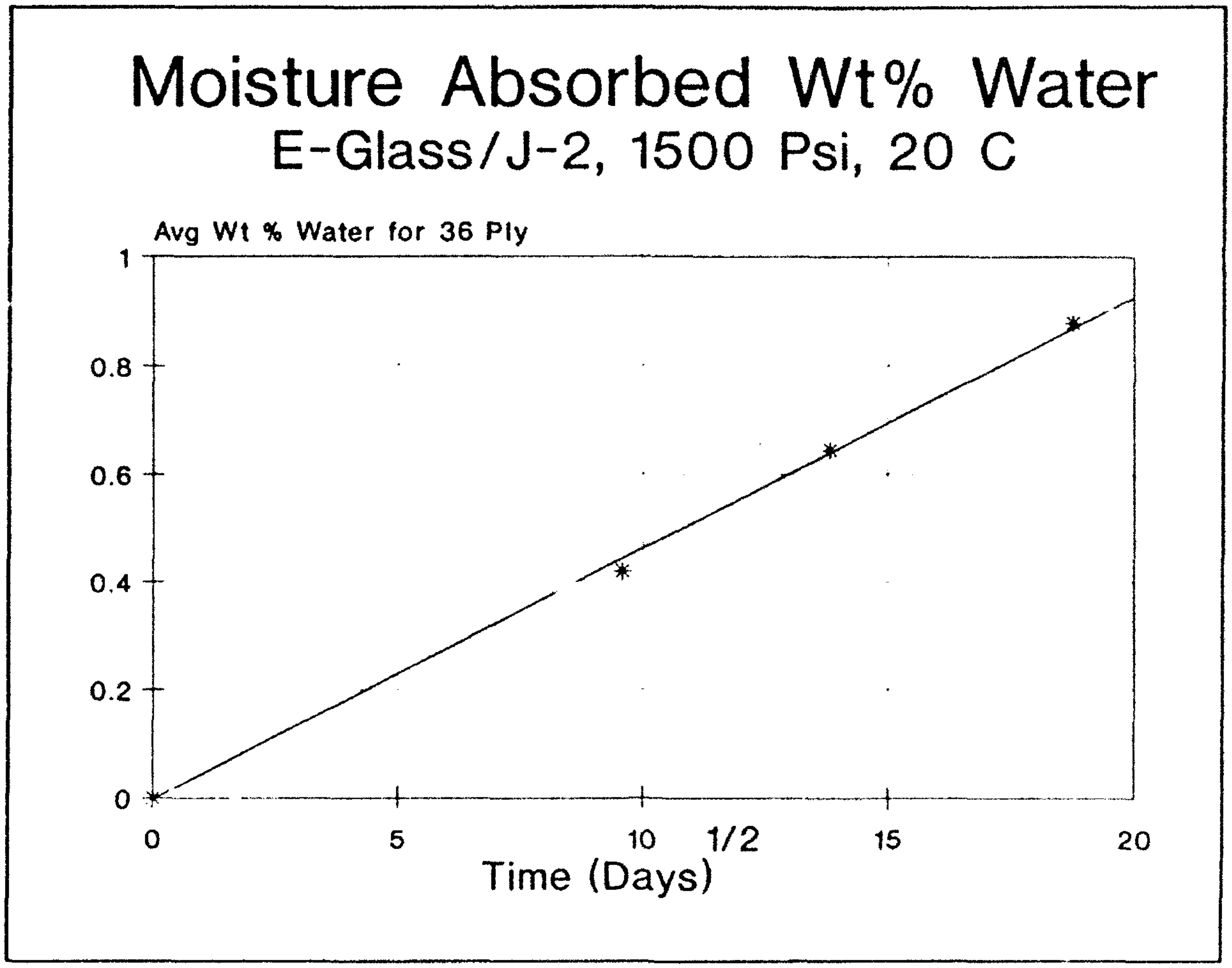


Figure 5 Moisture Absorbed Wt% Water

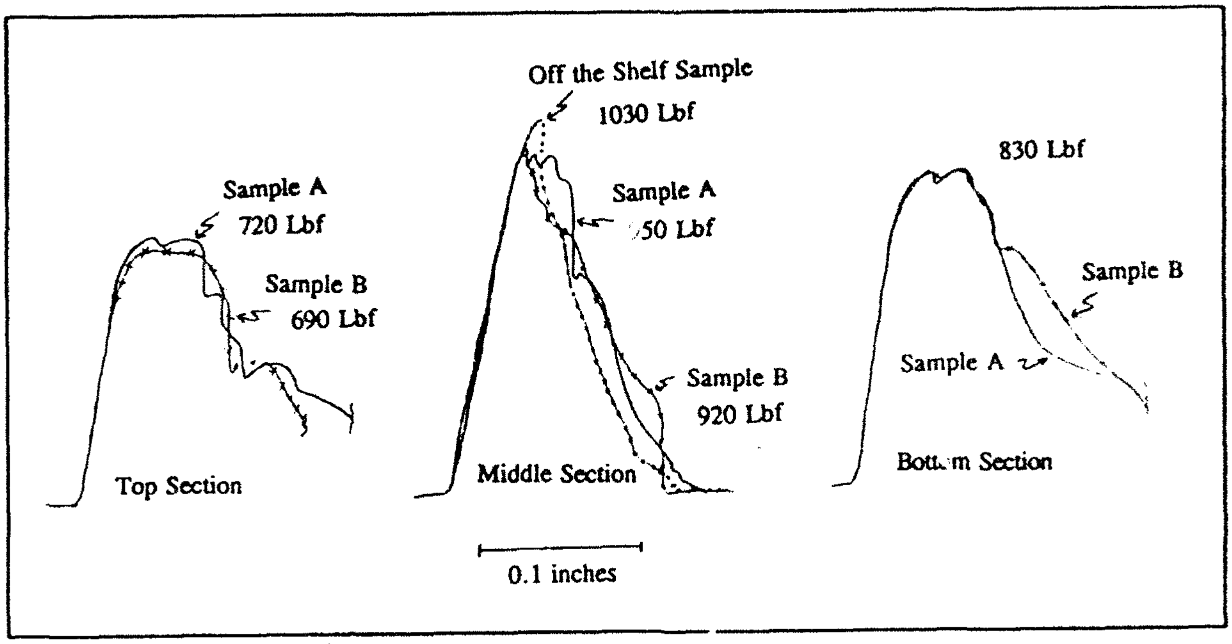


Figure 6 Load versus Flexure Traces

maximum load (maximum variation for maximum load; top section 4%, middle section 3%, bottom section 1%) to the trace of the one freeze/thaw control sample B. However, depending on specimen location (top, middle, or bottom) the maximum load is different, as shown in figure 6.

The average maximum load of 4.1 kN for off the shelf control samples were comparable to the middle section, of both the 15 cycle and one cycle freeze/thaw samples with the top section showing the lowest maximum load, average maximum load 3.0 kN or -27%, and the bottom section, average maximum load 3.7 kN lbs or -10%, being greater than the top and less than the middle section, as shown in figure 7. The corresponding stress levels are 68.7, 50.0, and 61.5 MPa for the mid, top and bottom positions respectively. This difference in maximum load between the top and bottom suggest that the bottom section contact patch with the bottom of the pressure chamber reduced the available area for water intrusion. The samples were oriented in the chamber but not placed in any special configuration to determine the size of the contact patch at the bottom of each sample.

The maximum stress values above compare to those of Juska (3) who reported values of 70.3 MPa and 58.6 MPa for dry material and for 1.24 wt% moisture absorption materials, respectively.

After the initial immersion of 369 days, the ends of the specimens exhibited partial opacity in ambient light for approximately 10-15% of the sample length. This seemed to increase after the second immersion, but did not increase after subsequent immersions. This opacity is probably related to the diffusion of the moisture along the fiber/matrix interface.

Fractography

Fractured SBS specimens from the top and bottom of the freeze/thaw samples A and C exhibited multiple delaminations as illustrated by the "end on" macrographs in figure 8, while the SBS specimens from the single freeze/thaw cycle, sample B, show only a single delamination. Also, it should be noted that for SBS specimens from the middle of all freeze/thaw samples and all SBS specimens from the dry "off the shelf" samples delaminations were not observed at fracture. This result suggest that significant moisture absorption did not occur in the mid section of the freeze/thaw samples. Further, diffusion of water was primarily through the ends, and it probably occurred along the fiber/matrix interface.

CONCLUSIONS

From the data and observations gathered, freeze/thaw cycles on E-glass/J-2 matrix composite does not appreciably decrease the maximum load characteristics. However the location of the short beam shear specimens (ie, top middle, bottom) taken from the hydrostatically conditioned sample does effect the load characteristics of this composite after long term immersion in simulated saltwater. For example the middle section piece has a maximum load very similar to the dry samples (5% difference in average between maximum loads of "off the shelf samples" and middle section of all freeze/thaw specimens).

The observation that the freeze/thaw specimens failed with multiple delaminations and the dry or refrigerated samples failed with single delaminations warrants further investigation.

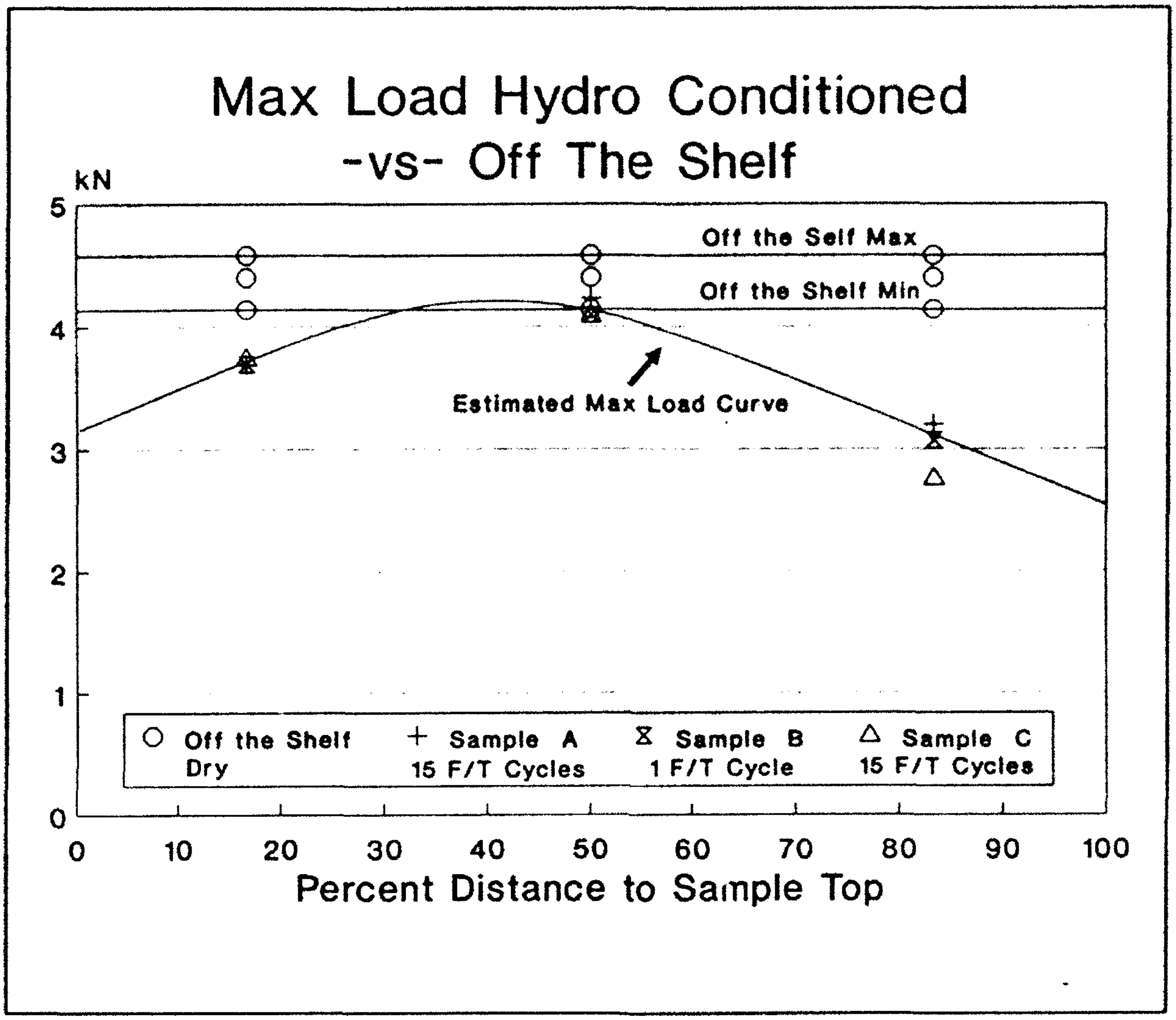
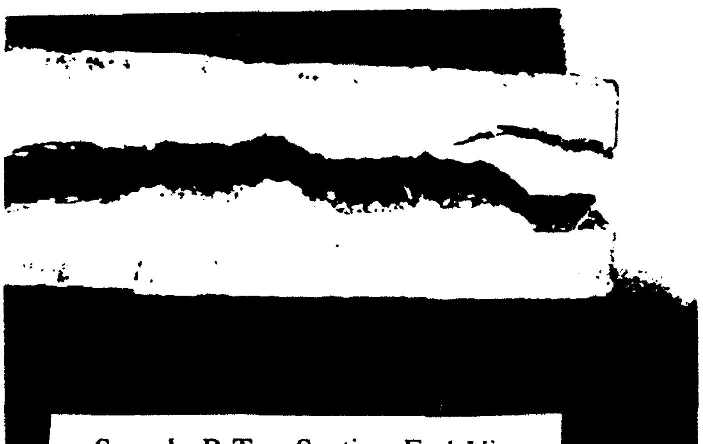
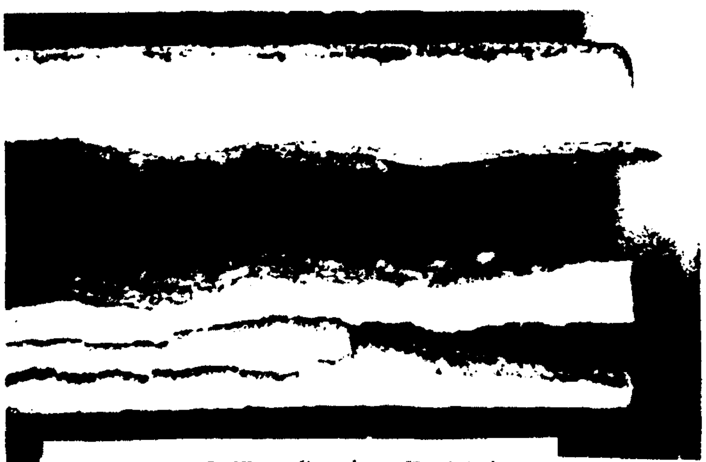


Figure 7 Maximum Load versus Sample Section Location

Sample A Top Section End View



Sample B Top Section End View



Sample C Top Section End View

Figure 8 Macroscopic Fracture Delamination

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